PATENT SPECIFICATION (11) 1 547 307

1 547 307

(21) Application No. 7609/77 (22) Filed 23 Feb. 1977 (19)
(31) Convention Application No. 660 672
(32) Filed 23 Feb. 1976 in
(33) United States of America (US)
(44) Complete Specification published 6 June 1979
(51) INT CL² C07F 9/09; C08K 5/52
(52) Index at acceptance
C2P 1L1 3B11A 3B15A 3B18B 3B21 C D
C3K 221 222 252 EA
C3R 32B1B 32B2A2 32D16C 32D16D 32D6A 32D6C 32D6D 32D6K 32E1 32G1Y 32H1 32H5B2 32H5BY 32H6A, 32H6Y 32H8 32J2E 32J2F 32J2Y 32KH 32P5A2 32P5AY C10 C12 C13P C23 L1B L2CX L4C

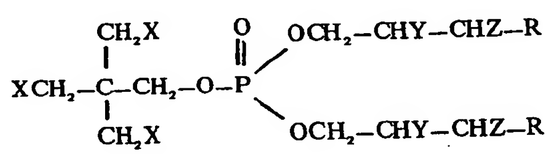
(54) HALOALKYL PHOSPHATES WITH INCREASED HYDROLYTIC STABILITY

(71) We, VELSICOL CHEMICAL CORPORATION, a corporation organised and existing under the laws of the State of Delaware, United States of America, of 341 East Ohio Street, Chicago, Illinois 60611, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to haloalkyl phosphates with increased hydrolytic stability.

The use of haloalkyl phosphates as flame retardants is known, see U.S. Patent Specifications Nos. 3,132,169; 3,287,266; 3,324,205; and 3,830,886.

According to the present invention there are provided compounds of the formula (I)



(I)

wherein

each of the X symbols, which may be the same or different, represents a hydrogen, chlorine or bromine atom,

the Y symbols are the same and both represent chlorine or bromine atoms,

each of the Z symbols, which may be the same or different, represents a chlorine or bromine atom, and

each of the R symbols, which may be the same or different, represents a hydrogen atom, an alkyl group containing 1 to 3 carbon atoms or a haloalkyl group containing 1 to 3 carbon atoms and 1 to 3 halogen atoms selected from chlorine and bromine.

It has been found that the compounds of formula I, which are haloalkyl phosphates, possess increased hydrolytic and thermal stability compared with other haloalkyl phosphates. This improved hydrolytic and thermal stability enables the haloalkyl phosphates of this invention to impart flame retardancy of increased durability to materials treated therewith.

Preferably in the compound of formula I the R symbols are the same and more preferably both the R symbols represent hydrogen atoms.

Preferably each of the X symbols, which may be the same or different, represents a chlorine or bromine atom or two of the X symbols represent hydrogen atoms and the other represents a chlorine or bromine atom.

It is also preferred that the Z symbols be the same halogen as the Y symbols. Further Y is preferably bromine.

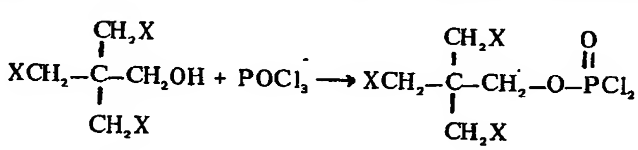
Preferred compounds of formula I include bis(2,3-dibromopropyl)-3-bromo-2,2-bis(bromomethyl)propyl phosphate, bis(2,3-dibromopropyl)-3-bromo-2,2-bis(methyl)-propyl phosphate, bis(2,3-dibromopropyl)-3-chloro-bis(bromomethyl)propyl phosphate, bis(2,3-dibromopropyl)-3-chloro-2,2-bis(chloromethyl)-propyl phosphate, bis-(2,3-dibromopropyl)-3-chloro-2,2-bis(methyl)propyl phosphate, and bis(2,3-dichloro-propyl)-3-chloro-2,2-bis(methyl)propyl phosphate.

Exemplary compounds of formula I are also listed in Table I below:

TABLE I

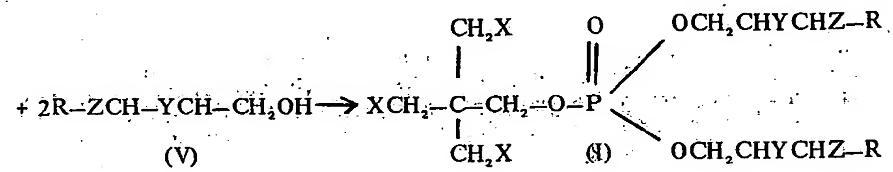
Compound	X	X	X	Y	Y	Z	Z	R	R
1	Br	Br	Br	Br	Br	Br	Br	H	H
2	Cl	H	H	Br	Br	Br	Br	H	H
3	Cl	Br	Br	Br	Br	Br	Br	H	H
4	Cl	Cl	Cl	Br	Br	Br	Br	H	H
5	Br	Br	H	Br	Br	Br	Br	H	H
6	Cl	H	H	Cl	Cl	Cl	Cl	H	H
7	Cl	Cl	Cl	Cl	Cl	Cl	Cl	H	H
8	Br	Br	Br	Cl	Cl	Br	Br	H	H
9	Cl	H	H	Cl	Cl	Br	Br	H	H
10	Cl	Cl	Cl	Cl	Cl	Cl	Br	H	H
11	Br	Br	Br	Br	Br	Br	Cl	H	H
12	Br	H	H	Br	Br	Br	Br	H	H
13	H	H	H	Br	Br	Br	Br	H	H
14	H	H	H	Cl	Cl	Cl	Cl	H	H
15	Br	H	H	Cl	Cl	Cl	Cl	H	H
16	Br	Br	Br	Br	Br	Br	Cl	$(CHBr)_2CH_2Br$	CH_3
17	Cl	H	H	Cl	Cl	Cl	Cl	CH_2Cl	CH_2Cl
18	Cl	Br	Br	Br	Br	Br	Br	$CHBrCH_2Br$	$CHBrCH_2Br$
19	Cl	Cl	Cl	Br	Br	Br	Br	$(CHBr)_2CH_2Br$	$(CHBr)_2CH_2Br$
20	Br	Br	H	Br	Br	Br	Br	CH_2Br	CH_2Br

The compounds of formula I may be prepared according to the following reaction scheme:



(III) (IV)

Equation A



Equation B

wherein X, Y and Z and R are as defined above.

More particularly, the reaction of Equation A is generally carried out by the reaction of equimolar quantities of the desired substituted neopentyl alcohol of formula III with phosphoryl chloride. The reaction can be carried out at a temperature between 0° to 150°C. and preferably from 60° to 120°C using magnesium oxide or a metal salt catalyst, e.g. titanium tetrachloride, calcium chloride and magnesium chloride. The reaction can also be carried out using an equimolar quantity of an organic tertiary amine base as a catalyst and hydrogen chloride acceptor, e.g. triethylamine and pyridine. Similarly, reaction of a metal salt of the alcohol of formula III with phosphoryl chloride results in the desired product. The reaction is generally carried out from 1 to 48 hours but the time is dependent on the reaction temperature. For convenience, reaction times of 1 to 8 hours are generally used.

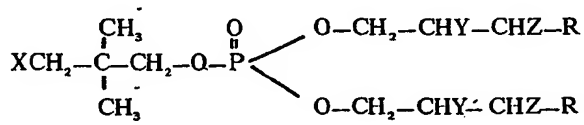
Also more particularly, the reaction of Equation B is generally carried out by the reaction of 2 moles of the substituted 2-haloalkanol of formula V with one mole of the substituted neopentyl dichlorophosphate of formula IV prepared according to Equation A. The reaction of Equation B can be carried out without isolation or purification of the intermediate chlorophosphate and is generally carried out under the same conditions as the first reaction. The resulting phosphates may be purified by washing with dilute base to remove acidic by-products, followed by steam distillation to remove volatile by-products. The products are dried, decolourised and filtered.

The compounds of formula I may be used as flame retardants in polymeric compositions selected from the group consisting of polyurethanes, including flexible and rigid foams and elastomers, polyesters, both saturated and unsaturated polyesters, and styrene polymers such as polystyrene, including both crystalline and high impact types, and styrene co- and terpolymers such as styrene-butadiene copolymer, styrene-acrylonitrile copolymer and acrylonitrile-butadiene-styrene terpolymers. A further description of above polymers applicable to the present invention may be found in Modern Plastics Encyclopedia, Vol. 52, No. 10A, McGraw-Hill, Inc., New York, New York (1975).

The compounds of formula I also possess good flame retardant efficacy in polyolefins, e.g., polypropylene and polyethylene. A detailed description of polyolefin polymers can be found in Modern Plastics Encyclopedia, ibid.

The compounds of this invention may be incorporated into or applied onto flammable polyurethane, polyester, and styrene polymeric material by techniques which are standard or known to those skilled in the art. See, for example, J. M. Lyons, "The Chemistry and Uses of Fire Retardants", Wiley-Interscience, New York, NY (1970), and Z. E. Jolles, "Bromine and Its Compounds", Academic Press, New York, NY (1966).

A particularly preferred group of compounds of this invention are those of the formula II:



(II)

wherein X represents a chlorine or bromine atom and Y, Z, and R, as well as their preferred embodiments, are as defined above. The compounds of formula II are preferred because they combine the increased hydrolytic and thermal stability possessed by the compounds of this invention with a relatively low viscosity to produce a flame retardant compound which is excellent for use in polymeric systems wherein the viscosity of the flame retardant and/or its hydrolytic and/or thermal stability are important factors, e.g., polyurethanes. A relatively low viscosity greatly enhances a flame retardant's ease of handling by enabling the flame retardant to be pumped under less severe conditions

of pressure and heat. For halogenated flame retardants of the same thermal stability, the difference in viscosity enables the lower viscosity flame retardant to be handled at a given viscosity while being subjected to less heat, thereby saving energy as well as prolonging the pot life of the polymeric composition containing the lower viscosity flame retardant because the rate at which the flame retardant decomposes is reduced. Further, a lower viscosity flame retardant will also mix more rapidly with a given polymer.

Depending on the substrate and the amount of flame retardancy desired, up to about 40 weight percent of the compound of formula I can be incorporated therewith. However, in most applications, it is preferred to use less than 25 weight percent of the compounds of formula I. It should be noted that the optimum level of additive of formula I depends upon the particular substrate being treated as well as the level of flame retardancy desired. For example, in polyesters a flame retardant level of from 10 to 35 percent by weight of the total polymeric composition is satisfactory.

In addition to the compounds of formula I, the flame retardancy of a polymer can be further enhanced through the use of so-called "synergists" or enhancing agents which when used with the compounds of formula I promote a cooperative effect therebetween and thus enhance the flame retardancy of the resultant composition as compared to the flame retardancy of either component used separately. These "enhancing agents" comprise oxides and halides of groups IVB and VB of the Periodic Table, i.e. oxides and halides of antimony, bismuth, arsenic, tin, lead, germanium, e.g., antimony oxychloride, antimony chloride, antimony oxide, stannic oxide, stannic chloride, arsenous oxide and arsenous chloride; and organic and inorganic compounds of phosphorus, nitrogen, boron and sulphur, e.g. triphenyl phosphate, ammonium phosphate, zinc borate, thiourea, urea and stannic sulphide; and oxides and halides of titanium, vanadium, chromium, manganese, iron, niobium, molybdenum, copper, zinc, magnesium, e.g., titanium dioxide, titanium chloride, vanadium pentoxide, chromic bromide, manganous oxide, molybdenum trioxide and ammonium molybdate; and hydrates of the above, e.g. stannic oxide hydrate, lead hydrate; and combinations thereof. The preferred enhancing agents are the oxides of antimony, arsenic and bismuth. However, any compound which on decomposition, as by ignition, yields these oxides would be suitable. Thus some organic antimonates are also preferred. The enhancing agents described in U.S. Patent Specification No. 3,205,196 are also suitable for use.

U.S. Patent Specification No. 3,205,196, column 2, states that antimony oxide is the antimony compound that is presently preferred for use in the invention disclosed therein. However, many antimony compounds are suitable. Inorganic antimony compounds include antimony sulphide, sodium antimonite, potassium antimonite, and the like. Many organic antimony compounds are suitable such as the antimony salts of organic acids and their pentavalent derivatives disclosed in U.S. Patent Specification No. 2,996,528. Compounds of this class include antimony butyrate, antimony valerate, antimony caproate, antimony heptylate, antimony caprylate, antimony pelargonate, antimony caprate, antimony cinnamate, antimony anisate, and their pentavalent dihalide derivatives. Likewise, the esters of antimonous acids and their pentavalent derivatives disclosed in U.S. Patent Specification No. 2,993,924, such as tris(n-octyl) antimonite, tris(2-ethylhexyl) antimonite, tribenzyl antimonite, tris(β-chloroethyl) antimonite, tris(β-chloropropyl) antimonite, tris(β-chlorobutyl) antimonite and their pentavalent compounds are the cyclic antimonites such as trimethylolpropane antimonite, pentaerythritol antimonite, and glycerol antimonite. The corresponding arsenic and bismuth compounds can also be employed. It it to be understood that the enhancing agents of U.S. Patent Specifications Nos. 3,205,196, 2,996,528 and 2,993,924 are also suitable for use with the compounds of formula I.

Preferred enhancing agents include Sb_2O_3, $SbCl_3$, $SbBr_3$, SbI_3, $SbOCl$, As_2O_3, As_2O_5, $ZnBO_4$, $BaB_2O_4.H_2O$, $2.ZnO.3B_2O_3.3.5H_2O$ and stannic oxide hydrate. The most preferred enhancing agent is antimony trioxide.

The polymer compositions containing the compound of formula I may also contain other materials where one desires to achieve a particular end result. Such materials include, adhesion promotors; antioxidants; antistatic agents; antimicrobials; colourants; other flame retardants such as those listed on pages 665—668; Modern Plastics Encyclopedia, ibid., (in addition to the flame retardants described herein); heat stabilisers; light stabilisers; pigments; plasticisers; preservatives; ultraviolet stabilisers and fillers.

In this last category, i.e. fillers, there can be mentioned materials such as glass, carbon; cellulosic fillers (wood flour, cork and shell flour); calcium carbonate (chalk, limestone, and precipitated calcium carbonate); metal flakes; metallic oxides (aluminium, beryllium oxide and magnesia); metallic powders (aluminium, bronze, lead, stainless steel and zinc); polymers (comminuted polymers and elastomerplastic blends);

silica products (diatomaceous earth, novaculite, quartz, sand, tripoli, fumed colloidal silica, silica aerogel, wet process silica); silicates (asbestos, kaolinite, mica, nepheline, syenite, talc, wollastonite, aluminium silicate and calcium silicate); and inorganic compounds such as barium ferrite, barium sulphate, molybdenum disulphide and silicon carbide.

The above mentioned materials, including fillers, are more fully described in Modern Plastics Encyclopedia, ibid.

The above described materials employed in the present compositions can be in any quantity which will not substantially adversely affect the desired results derived from the present compositions. Thus, the amount used can be any amount up to that percent based on the total weight of the composition at which the composition can still be classified if so desired as a plastic. In general, such amount will be from 0% to 75% and more specifically from 1% to 50% by weight.

The following Examples further illustrate the present invention. Unless otherwise specified, all temperatures are expressed in degrees centigrade; all weights are expressed in grams; and all volumes are expressed in milliliters.

Example 1.

Preparation of compound 1 of Table I:

A mixture of 650 grams of tribromoneopentyl alcohol, 307 grams of phosphoryl chloride and 3 grams of magnesium oxide was heated and stirred at 85° to 90°C. for three hours. After cooling overnight, 854 grams of 2,3-dibromopropanol were added and heated to about 85°C. for six hours. After aspirating at 95°C. for 0.5 hours, the product was washed three times with an aqueous ammonia solution having a pH of 8 and a temperature of 50°C. The volatile by-products were removed by steam distillation and the product was dried, treated with celite and celkate and filtered. A yield of 1200 grams (74%) of a viscous liquid was obtained. Analysis: Calculated for $C_{11}H_{18}Br_7O_4P$: Br, 69.48. Found: Br, 69.03.

Example 2.

Preparation of compound 3 of Table I:

A mixture containing 872 grams of 3-chloro-2,2-bis(bromomethyl)propyl dichlorophosphate and 900 grams of 2,3-dibromopropanol was heated to about 85°C. and allowed to react at that temperature for about six hours. After aspirating at 95°C. for 0.5 hours, the product was washed three times with an aqueous ammonia solution having a pH of 8 and a temperature of 60°C. The volatile by-products were removed by steam distillation and the product was dried, treated with celite and celkate, and filtered. A yield of 1308 grams of a viscous liquid was obtained. Analysis: Calculated for $C_{11}H_{18}Br_6ClO_4P$: Br, 63.4; Cl, 4.69. Found: Br, 62.24; Cl, 5.60.

Example 3.

Compound 2 of Table I was prepared in a manner similar to Example 2, except that 1400 g of 3 chloro-2,2-di(methyl)propyl dichlorophosphate was reacted with 2478 g of 2,3-dibromopropanol to yield 2355 g of a low viscosity liquid. Analysis: Calculated for $C_{11}H_{20}Br_4ClO_4P$: Br, 53.1; Cl, 5.90. Found: Br 51.0; Cl, 7.08.

Example 4.

Compound 4 of Table I was prepared in a manner similar to Example 2, except that 234 g of tris-2,2,2-(chloromethyl)ethyl dichlorophosphate was reacted with 305 g of 2,3-dibromopropanol to yield 366 g of a viscous liquid. Analysis: Calculated for $C_{11}H_{18}Br_4Cl_3O_4P$: Br, 47.6; Cl, 15.9. Found: Br, 47.72; Cl, 16.27.

Bis(2,3-dibromopropyl)-3-bromo-2,2-bis(methyl)propyl phosphate and bis(2,3-dichloropropyl)-3-chloro-2,2-bis(methyl)propyl phosphate as well as other compounds within the scope of formula I can be prepared in a manner similar to that employed in Examples 1 to 4.

Example 5.

A test, hereinafter referred to as the Hydrolytic Stability Test (HST), has been devised to quantitatively measure the hydrolytic stability of compounds. As applied to the compounds under consideration, the HST measures the extent to which the following reaction proceeds:

$$R_1O-\overset{\overset{O}{\|}}{\underset{\underset{OR_2}{|}}{P}}-OR_3 \xrightarrow{H_2O} R_1O-\overset{\overset{O}{\|}}{\underset{\underset{OR_2}{|}}{P}}-OH + R_3OH$$

Equation C

wherein R_1, R_2 and R_3 are independently selected from halogenated or unhalogenated carbon containing groups. The acid or Hydrolytic Stability Test Number (HST Number) is directly proportional to a compound's hydrolytic instability.

In particular, a magnetically stirred emulsion containing 4 grams of compound 1 of Table I, 1 gram of an emulsifier (Emcol AM2—10C, Witco Chemical Corporation, Organics Division, New York, New York), and 45 grams of water was heated at 100°C. for 44 hours. (The emulsifier is used merely for the purpose of obtaining a uniform emulsion of two otherwise immiscible liquids.) The HST Number of the emulsion as determined by titration with a standard potassium hydroxide solution was 1.81.

Using the HST described in Example 5, the hydrolytic stability of triethyl phosphate, bis(bromopropyl)chloroethyl phosphate, tris(2-chloroethyl)phosphate, tris(2,3-dibromoproprpyl)phosphate, and compound 2 of Table I was also determined. The HST Numbers for these compounds are listed in Table II.

TABLE II

Compound	HST Number (mg KOH/g Sample)
Triethyl phosphate	17.2
Bis(bromopropyl)chloroethyl phosphate	9.72
Tris(2-chloroethyl)phosphate	8.7
Tris(2,3-dibromopropyl) phosphate	3.2
Compound 2 of Table I	1.85
Compound 1 of Table I	1.81

Table II shows that bis(2,3-dibromopropyl)-3-chloro-2,2-bis(methyl)propyl phosphate and bis(2,3-dibromopropyl)-3-bromo-2,2-bis(bromomethyl)propyl phosphate have better hydrolytic stability than the prior art compounds.

Example 6.

Two flame retardant emulsions were prepared. The components of each emulsion and weight percent of each component are listed in Table III.

TABLE III

Component	Emulsion X	Emulsion Y
Water	60.0	60.0
Emulsion Concentrate	40.0	40.0
Compound 3, Table I	50.0	—
Bis(bromopropyl) chloroethyl phosphate	—	50.0
Solvent[a]	40.0	40.0
Emulsifying Agent[b]	10.0	10.0

a The solvent had a flash point of about 110°F. and a boiling point of about 315°F. (Hi-Sol 10 brand solvent, Ashland Chemical Company, Columbus, Ohio).

b The emulsifying agent was an anionic blend of oil-soluble metal sulfonates with polyoxyethylene ethers having an HLB value of 12.5. (Emcol N-141 brand emulsifying agent, Witco Chemical Co., Inc., Chicago, Illinois).

Two sets of samples of 100% polyester fabrics (Style Number 755H, 100% Spun Dacron 54, 36 × 32 count, 20/2 yarn size, 5.2 ounces per square yard, Testfabrics, Inc., Middlesex, New Jersey) were treated with the above emulsions. The processes to which the two sets of samples were subjected as well as the data obtained from the samples are listed in Table IV.

TABLE IV

Emulsion	Wet Pick Up, Percent	Processing			Br_2[d] Count	O_2[e] Index
		Dry[a]	Cure[b]	AW[c]		
X	72.0	X			14,012	
X	72.0	X	X		15,836	
X	72.0	X	X	X	15,268	30.0
Y	64.7	X			11,086	
Y	64.7	X	X[f]		2,552	
Y	64.7	X	X[f]	X	1,163	22.5
Control	—	—	—	—	—	22.5

a Dry: 5 minutes at 110°C.

b Cure: 90 seconds at 205°C.

c Afterwash: 40 grams of soda ash and 20 grams of Triton QS–44 detergent (Triton QS–44 is a trademark of Rohm and Haas Company, Philadelphia, Pennsylvania) were used with a Kenmore 600 washing machine on a delicate cycle, hot water (71°C.) and warm rinse setting. The samples were tumble-dried.

d Bromine count was obtained by the use of a fluorescent x-ray technique. When measuring the bromine content of identical fabric substrates as was the case herein, the bromine count is a relative number indicative of the bromine content of the fabric sample. This bromine count technique is basically a linear relation wherein the higher the bromine count the higher the bromine content of the fabric sample.

e Oxygen Index: ASTM D 2863–70.

f Observation: Tremendous fumes came out during and after the curing.

Table IV clearly indicates that the thermal stability of a flame retarding agent is decisive in the durability of a given flame retardant finish. The two emulsions contrasted in Table IV differ from each other solely in the flame retarding agent employed. Emulsion Y which employed a prior art flame retarding agent severly decomposed during the curing procedure, as evidenced by the bromine count as well as the tremendous amount of fumes observed during said procedure, and much of the emulsion finish was also removed during the afterwash step. Both of these phenomena are directly related to the relatively poor hydrolytic and thermal stability of the prior art flame retarding agent, bis(bromopropyl)chloroethyl phosphate, employed in Emulsion Y. In contrast, fabrics treated with Emulsion X containing a flame retarding agent within the scope of this invention maintained their bromine count throughout the drying, curing, and afterwash procedures. This stability of Emulsion X is due to the increased hydrolytic and thermal stability of the compounds within the scope of this invention. The superior oxygen index of the fabric treated with Emulsion X containing an exemplary flame retardant compound within the scope of this invention over the fabric treated with Emulsion Y containing a prior art flame retardant exemplifies the commercial importance of the increased hydrolytically and thermally stable compounds of this invention.

Example 7.

A solution of 600 grams of polystyrene and 10 parts per hundred resin (phr) of compound 3 of Table I in 2670 grams of methylene chloride and 60 grams of hexane was prepared. To the above solution was added 3 grams of dicumyl peroxide as a flame retardant synergist. This mixture was poured into an aluminium dish and the methylene chloride was allowed to evaporate in the air. Following this, the casting was steamed to produce a crude foam. This foam was then cut into sufficient specimens of appropriate sizes in order to subject the foam to three tests capable of measuring the non-flammability of said foam. The flammability tests to which the foam specimens were subjected consisted of the Underwriters' Laboratories, Inc.'s UL—94 Standard for Safety (UL—94)., ASTM D 2863—70 Oxygen Index Test (OI), and an ignition test (described below). The first two of the above tests are well known to those skilled in the art of flame retardants and therefore no elaboration on or summary of said tests is made herein. The ignition test entailed holding a foamed specimen in a vertical position and igniting said specimen for a second or so with a micro burner. To pass this ignition test the ignited foamed specimen upon removal of the ignition source, should cease burning in one second or less. The results obtained by subjecting the foamed specimens to the several flammability tests are listed in Table V.

Additional samples of polymer were prepared in which the amount of fire retardant was 2.5 phr and 5 phr. Still additional samples were prepared with the prior art compound tris(2,3-dibromopropyl)phosphate at the 2.5, 5 and 10 phr levels. These samples were tested in the same manner and the results obtained are also tabulated in Table V.

TABLE V

Flame Retardant	phr	OI	UL—94	Ignition Test
Compound 3, Table I	10	30.1	V—0	Pass
do	5	28.5	V—0	Pass
do	2.5	25.5	V—2	Pass
Prior Art				
Tris(2,3-dibromopropyl)phosphate	10	33.0	V—0	Pass
do	5	29.5	V—0	Pass
do	2.5	28.0	V—2	Pass

As exemplified by bis(2,3-dibromopropyl)-3-chloro-2,2-bis(bromomethyl)propyl phosphate in Table V, the flame retardants of this invention, e.g., bis(2,3-dibromopropyl)-3-bromo-2,2-bis(bromomethyl)propyl phosphate, bis(2,3-dibromopropyl)-3-bromo-2,2-bis(methyl)propyl phosphate, bis(2,3-dibromopropyl)-3-chloro-2,2-bis-

(chloromethyl)propyl phosphate, bis(2,3-dibromopropyl)-3-chloro-2,2-bis(methyl)-propyl phosphate, and bis(2,3-dichloropropyl)-3-chloro-2,2-bis(methyl)propyl phosphate, possess a flame retardant efficacy comparable to that of tris(2,3-dibromopropyl)-phosphate. However, it is known that the polymerization of styrene beads via a suspension system is a sensitive procedure. "The stability of the suspension system depends upon the selection of the suspending agent, the degree of agitation, the surface tension of the water, the parameter of the kettle, the condition of the water that is charged initially to the process, and many other factors, such as the time and the temperature in the reaction conditions. Because of all these variables, the stability of the suspension system is extremely important, not just for successful operation of the suspension system without failure and coalescence but also to guarantee an effective beadsize distribution of the final product which emerges from the kettles." R. B. Bishop, "Practical Polymerization for Polystyrene," 266, Cahners Books, Boston, Massachusetts 02116, 1971. The hydrolytic and thermal stability of flame retardant compounds is a variable which can adversely affect the stability of the suspension system. The higher a compound's HST Number, the more hydrolytically unstable that compound is and the more acidic and corrosive would be a solution or suspension containing said compound. This increase in acidity detrimentally affects the stability of the styrene suspension system; and because of its corrosive properties, decreases the useful life of process equipment. Therefore, the flame retardants within the scope of this invention introduce into the styrene suspension system more hydrolytically stable flame retardants thereby better assuring the stability of said styrene suspension system while maintaining the flame retardant efficacy of prior art flame retardants.

The following Examples exemplify other embodiments using compounds of formula I wherein the hydrolytic stability of the compounds makes a significant commercial difference.

Example 8.

The foam was prepared using the following basic formulation:

Component	Parts by Weight
Polyol[a]	100
Silicone Glycol[b] Surfactant	2
Trichlorofluoromethane[c]	35
Polyisocyanate[d]	135

[a]alkanolamine polyol, molecular weight approximately 3500, hydroxyl number approximately 530, Thanol R—350—X, Jefferson Chemical Co., Houston, Texas.
[b]Dow Corning 193, Dow Corning Corp., Midland, MI.
[c]Freon 11B, E. I. DuPont de Nemours & Co., Wilmington, Del.
[d]Polymeric aromatic isocyanate, 31.5% available NCO, Mondur MRS, Mobay Chemical Co., Pittsburgh, PA.

The polyol, surfactant, and fluorocarbon blowing agent were combined in a masterbatch based on 1000 g of polyol to minimize loss of blowing agent.

The following procedure was used to prepare the foam:

1. The polyisocyanate was weighed into a tared, 10 ounce, paper cup (allowances being made for hold-up) and the cup set aside while the remaining ingredients were weighed out and mixed.
2. The polyol masterbatch was weighed out, in the proper amount to give 100 grams of polyol, in a one quart, untreated, paper cup.
3. The 10 grams of Compound 3 of Table I were then weighed into the same one quart cup.
4. The contents of the one quart cup were mixed at 1000 rpm for 5 seconds.
5. The polyisocyanate was then added and stirring at 1000 rpm continued for 10 seconds.
6. The mix was poured into a 5 pound, untreated, paper tub and allowed to rise.

After the foam was tack-free, and substantially cured, it was set aside for at least seven days before cutting the foam in half to observe the extent of "scorch" (discoloration) at the center. These observations are recorded in Table VI.

Using the same procedure other foams were made at different load levels as well as containing different flame retardant additives. The results of these additional tests are also reported in Table VI.

TABLE VI

Flame Retardant	phr	Scorch	OI
(control)	—	None Detected	20.5
Compound 5, Table I	10	None Detected	23.5
do	20	None Detected	25.5
do	30	None Detected	26.5
Compound 6, Table I	10	None Detected	22.5
do	20	None Detected	23.5
do	30	None Detected	24.5
(Prior Art) tris(2,3-dibromopropyl)phosphate	10	Pronounced Scorch	23.5
do	20	Pronounced Scorch	25.5
do	30	Pronounced Scorch	26.5

The presence of scorch is detrimental for basically three reasons. First, scorch is not aesthetic in appearance and is therefore a very undesirable property in foams whose ultimate application necessitates their use as cuttings. Second, industrial manufacturers fear the presence of discoloration in the center of rigid polyurethane foams because at one time said discoloration was an indication that excessive heat was being generated inside the foam during the manufacturing process which could possibly result in the ignition of the rigid foams. Third, the presence of scorch is felt to be an indication of the decomposition of the flame retardant additives which decomposition detrimentally affects the physical properties of the foam.

Example 9.

Type I toluene diisocyanate (hereinafter referred to as TDI) was placed in a first tank of a Martin Sweets Modern Module No. 3A urethane foam equipment modified for six components. Compound 2 of Table I (1 kg) was mixed with 10 kg of Pluracol GP 3030 polyol in a second tank. (Pluracol GP 3030 brand polyol, BASF Wyandotte, Wyandotte, MI, is a polypropylene glycol having a molecular weight of approximately 3000 and a hydroxyl number of approximately 56.) Stannous octoate catalyst was placed in a third tank (T—9 brand catalyst, M & T Chemicals, Inc., New York, NY). Into a fourth tank was placed a silicone surfactant (L—540 brand silicone surfactant, Union Carbide Corp., New York, N.Y.). A water-triethylene diamine mixture (3/0.45) was added to a fifth tank. (Dabco 33LV brand triethylene diamine, Houndry Process & Chemical Co., is a 33% solution of triethylene diamine in dipropylene glycol.) All of the above components were simultaneously mixed using a size 3 pin type mixer at 3,000 rpm in the following ratio:

Component	Parts by Weight
Compound 2, Table I	10
Polyol	100
TDI	39.3
Stannous Octoate	0.16
Silicone surfactant	1.0
Water	3.0
Triethylene diamine	0.45

The mixture was dropped during the mixing procedure into a 14" × 14" × 6" Adstrom cardboard box. After the foam came to full height it was post cured in a forced air oven at 99° to 104°C. for 30 minutes.

After allowing the foam to sit for at least 7 days, the foam was then subjected to ASTM D 1564 Compression Set Method B—1971. The data obtained from this test is reported in Table IX.

The same procedure was used to make other foams at different load levels. Those foams were also subjected to the Compression Set Test and the data obtained reported in Table VII.

TABLE VII

Flame Retardant		90% Compression Set[a] (Parallel Rise)	
	phr	C_t[b]	C_d[c]
Control	—	6.98	7.75
Compound 2, Table I	10	4.23	4.70
do	20	14.9	16.5

a ASTM D–1564–1971 — Compression Set Test Method B.

b C_t is the compression set expressed as a percent of the original thickness

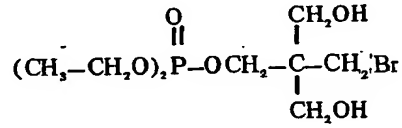
c C_d is the compression set expressed as a percent of the original deflection.

The higher the compression set number the poorer are the physical properties of the foam. Further, in order to pass ASTM D—1564 Compression Set Test Method B, a foam has to display a compression set number less than 20 percent. Therefore, as Table VII indicates, Compound 2 of Table I passes the ASTM test.

Other flame retardants within the scope of this invention, e.g., bis(2,3-dibromopropyl)-3-bromo-2,2-bis(bromomethyl)propyl phosphate, bis(2,3-dibromopropyl)-3-bromo-2,2-bis(methyl)propyl phosphate, bis(2,3-dibromopropyl)-3-chloro-bis(bromomethyl)propyl phosphate, bis(2,3-dibromopropyl)-3-chloro-2,2-bis(chloromethyl)-propyl phosphate, bis(2,3-dibromopropyl)-3-chloro-2,2-bis(methyl)propyl phosphate, and bis(2,3-dichloropropyl)-3-chloro-2,2-bis(methyl)propyl phosphate, also possess excellent flame retardant efficacy in polyurethane, polyester, and styrene polymeric compositions.

Example 10.

Using the exact procedure of Example III of U.S. Patent Specification No. 3,830,886, a compound was produced which is disclosed in said Example 3 to be 3-bromo-2,2-bis(hydroxymethyl)propyl diethyl phosphate of the formula



The viscosity of 3-bromo-2,2-bis(hydroxymethyl)propyl diethyl phosphate was determined at 28°C. using a Brookfield Viscosimeter. In the same manner the viscosity of Compound 2 of Table I was determined and the results are listed in Table VIII. Also listed in Table VIII is the viscosity of tris(2,3-dibromopropyl)phosphate, another prior art flame retardant.

TABLE VIII

	Viscosity, Centipoise	Viscosity Increase Over Compound 2, Table I (Percent)
3-bromo-2,2-bis-(hydroxymethyl)propyl diethyl phosphate	9450	497
tris(2,3-dibromopropyl)-phosphate	7500	395
Compound 2, Table I	1900	

As exemplified by bis(2,3-dibromopropyl)-3-chloro-2,2-bis(methyl)propyl phosphate, in Table VIII, compounds within the scope of formula II, e.g., bis(2,3-dibromopropyl)-3-bromo-2,2-bis(methyl)propyl phosphate and bis(2,3-dichloropropyl)-3-chloro-2,2-bis(methyl)propyl phosphate, possess a viscosity which is unobviously low in view of the prior art. This substantial decrease in the viscosity of formula II compounds has significant commercial implications in both flexible and rigid polyurethane foams as well as in any polymeric system wherein viscosity is a factor to be taken into consideration. The relatively low viscosity of compounds within the scope of formula II greatly enhances their ease of handling by enabling said flame retardants to be pumped under less severe conditions of pressure and heat. For halogenated flame retardants of the same thermal stability, the difference in viscosity enables the lower viscosity flame retardants within the scope of formula II of this invention to be handled at a given viscosity while being subjected to less heat, thereby saving energy as well as prolonging the pot life of the polymeric composition containing a polymer and said lower viscosity flame retardants because the rate at which the flame retardant breaks apart is reduced. Further, the lower viscosity flame retardants within the scope of formula II of this invention will also mix more rapidly with a given polymer.

Example 11.

The thermal stability of compound 4 of Table I, tris(2-chloroethyl)phosphate, and tris(2,3-dibromopropyl)phosphate was determined by the procedure set forth in Section 9—951, "Thermogravimetric Analyzer", of "Instruction Manual 990, Thermal Analyzer and Modules", E. I. Du Pont De Nemours and Co. (Inc.), Instrument Products Division, Wilmington, Delaware 19898. The results of the thermogravimetric analysis (TGA) of the three compounds at several different weight losses are tabulated in Table IX as follows:

TABLE IX

TGA RESULTS

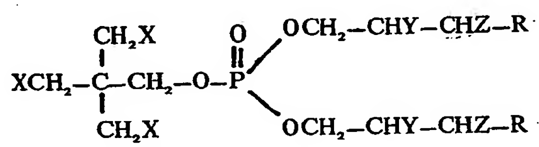
	Temperature at which weight Change Occurs, °C.		
Compound	10% wt. Loss	25% wt. Loss	50% wt. Loss
Compound 4, Table I	285	307	323
Tris(2-chloroethyl)-phosphate	182	197	209
Tris(2,3-dibromopropyl) phosphate	273	288	307

As exemplified by bis(2,3-dibromopropyl)-3-chloro-2,2-bis(chloromethyl)propyl phosphate, in Table IX, compounds within the scope of this invention, e.g., bis(2,3-dibromopropyl)-3-bromo-2,2-bis(bromomethyl)propyl phosphate, bis(2,3-dibromopropyl)-3-bromo-2,2-bis(methyl)propyl phosphate, bis(2,3-dibromopropyl)-3-chloro-bis(bromomethyl)propyl phosphate, bis(2,3-dibromopropyl)-3-chloro-2,2-bis(methyl)-propyl phosphate, and bis(2,3-dichloropropyl)-3-chloro-2,2-bis(methyl)propyl phosphate, possess superior thermal stability than that possessed by prior art compounds.

[The words CELITE, DACRON, KENMORE, THANOL, FREON, MONDUR, PLURACOL and DABCO are registered Trade Marks.]

WHAT WE CLAIM IS:—

1. A compound of the formula



(I)

wherein

each of the X symbols, which may be the same or different, represents a hydrogen, chlorine or bromine atom,

the Y symbols are the same and both represent chlorine or bromine atoms,

each of the Z symbols, which may be the same or different, represents a chlorine or bromine atom, and

each of the R symbols, which may be the same or different, represents a hydrogen atom, an alkyl group containing 1 to 3 carbon atoms or a haloalkyl group containing 1 to 3 carbon atoms and 1 to 3 halogen atoms selected from chlorine and bromine.

2. A compound according to claim 1 wherein both R symbols represent hydrogen atoms.

3. A compound according to claim 1 or 2 wherein each Y and Z symbol represents a bromine atom.

4. A compound according to any one of claims 1 to 3, wherein each of the X symbols, which may be the same or different, represents a chlorine or bromine atom.

5. A compound according to any one of claims 1 to 3, wherein two X symbols represent hydrogen atoms and the other X symbol represents a chlorine or bromine atom.

6. Bis(2,3-dibromopropyl)-3-bromo-2,2-bis(bromomethyl)propyl phosphate.

7. Bis(2,3-dibromopropyl)-3-bromo-2,2-bis(methyl)propyl phosphate.

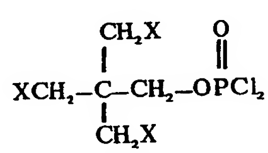
8. Bis(2,3-dibromopropyl)-3-chloro-bis(bromomethyl)propyl phosphate.

9. Bis(2,3-dibromopropyl)-3-chloro-2,2-bis(chloromethyl)propyl phosphate.

10. Bis(2,3-dibromopropyl)-3-chloro-2,2-bis(methyl)propyl phosphate.

11. Bis(2,3-dichloropropyl)-3-chloro-2,2-bis(methyl)propyl phosphate.

12. A process for preparing a compound as claimed in claim 1 which process comprises reacting one mole of a compound of formula IV



(IV)

(wherein X is as defined in claim 1) with two moles of a compound of formula V

$$R{-}CHZ{-}CHY{-}CH_2OH \qquad (V)$$

(wherein Y, Z and R are as defined in claim 1).

13. A process for preparing a compound as claimed in claim 1 substantially as described in any one of Examples 1 to 4.

14. A compound according to claim 1 prepared by the process claimed in claim 12 or 13.

15. A polymer composition comprising a polyurethane, polyester, styrene polymer or polyolefin and, as flame retarding agent, a compound as claimed in any one of claims 1 to 11.

16. A polymer composition comprising a polyurethane and, as flame retarding agent, a compound as claimed in claim 5.

Agents for the Applicants,
GALLAFENT & CO.,
Chartered Patent Agents,
8 Staple Inn,
London WC1V 7QH.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1979. Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.